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Preparation, Crystal Structure Analysis, and Catalytic Application of [(*S*)-BINAP]Ni(COD) and [(*S*)-BINAP]NiBr$_2$

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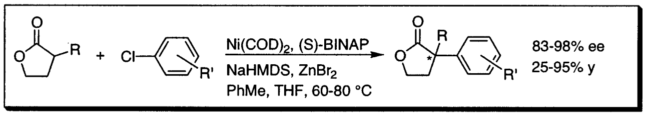
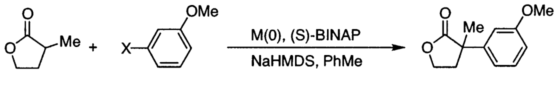
*Summary: The efficient preparation of [(S)-BINAP]Ni(COD) (**1**) and [(S)-BINAP]NiBr$_2$ (**2**) is reported. X-ray crystal structure analysis of these potential precatalysts provides the first structural insights into the nickel−BINAP system at both the 0 and +2 oxidation states.*



Introduction

Chiral bidentate phosphine ligands are ubiquitous in asymmetric catalysis.[1] Enantiopure 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), introduced by Noyori,[2] has repeatedly proven to be a highly efficient ligand in a diverse number of transition-metal-catalyzed, enantioselective transformations.[3] Recent developments have greatly facilitated the synthesis of BINAP and its derivatives, resulting in a broader application of these ligands in industry and academics.[4] While palladium−,[5] rhodium−,[6] and ruthenium−BINAP[7] systems comprise the majority of successful asymmetric catalytic reactions,[3] other metals have been utilized to a lesser degree. For example, there have been few reports[8] of successful nickel−BINAP catalyzed enantioselective transformations, despite the low cost of nickel and high reactivity of Ni(0) complexes toward aryl and vinyl chlorides.[9] Presumably, the relatively low binding affinity of Ni(0) with BINAP, which has been utilized in the synthesis of BINAP itself,[4a] in addition to the air sensitivity of Ni(0) complexes in general, detracts from its utility.



Entry	M(0)	X	Additive	Temp. (°C)	Yield(%) / ee (%)	Abs.config.
1	Ni(COD)$_2$	Br		60	29 / 99	(S)
2	Ni(COD)$_2$	Cl		60	40 / 95	(S)
3	Ni(COD)$_2$	Cl	ZnBr$_2$	60	86 / 95	(S)
4	Pd$_2$(dba)$_3$	Br		50	31 / 59	(R)

Conditions: 5 mol% of M(0). Entries 1-3: 8.5 mol% BINAP, entry 4: 15 mol% BINAP. ZnBr2 was added as a THF solution. Reaction time: 15-20h.

Figure 1. Enantioselective α-arylation of α-substituted γ-butyrolactones.

Recently, while investigating the enantioselective α-arylation of α-substituted γ-butyrolactones, we have found that 5 mol % of in situ generated [(*S*)-BINAP]Ni(COD) (**1**) in combination with ZnBr$_2$ constitutes a highly efficient catalytic system.[10] The quaternized products are isolated in excellent enantioselectivities and moderate to excellent yields.

Two points are worth noting. (i) The addition of 15 mol % ZnBr$_2$ as a THF solution is instrumental for the dramatic increase in the rate of the reaction, ultimately leading to a higher isolated yield of the product (Figure 1, entry 3). Initial findings suggest that ZnBr$_2$ acts as a Lewis acid, facilitating halide abstraction from the oxidative addition product [(*S*)-BINAP]Ni(Ar)(X). (ii) It was found that under similar conditions use of a Pd−(*S*)-BINAP catalyst provided the opposite enantiomer, albeit with lower enantioselectivity (entry 4). In our endeavor to gain further mechanistic and structural insight, we sought to prepare and characterize [(*S*)-BINAP]Ni(COD) (**1**) and [(*S*)-BINAP]NiBr$_2$ (**2**).

Results and Discussion

Reaction of Ni(COD)$_2$ with (*S*)-BINAP in toluene at room temperature results in the clean formation of [(*S*)-BINAP]Ni(COD) (**1**), which can be isolated in 65% yield

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[1] *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley: New York, 2000.

[2] Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932−7934.

[3] (a) Akutagawa, S. *Appl. Catal., A* **1995**, *128*, 171−207. (b) Kumobayashi, H.; Miura, T.; Sayo, N.; Saito, T.; Zhang, X. *Synlett* **2001**, 1055−1064.

[4] (a) Cai, D.; Payack, J. F.; Bender, D. R.; Hughes, D. L.; Verhoeven, T. R. Reider, P. J. *J. Org. Chem.* **1994**, *59*, 7180−7181. (b) Ager, D. J.; East, M. B.; Eisenstadt, A.; Laneman, S. A. *Chem. Commun.* **1997**, 2359−2360. (c) Cai, D.; Payack, J. F.; Bender, D. R.; Hughes, D. L.; Verhoeven, T. R.; Reider, P. J. *Org. Synth.* **1999**, *76*, 6.

[5] (a) Use of Pd−BINAP for the asymmetric Heck reaction: Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Sausalito, CA, 1999; Chapter 4.6. (b) Use of Pd−BINAP for the asymmetric allylic alkylation: ref 5a, Chapter 9.3.

[6] Use of Rh−BINAP for the asymmetric isomerization: Akutagawa, S. *Top. Catal.* **1998**, *4*, 271−274.

[7] Use of Ru−BINAP for the asymmetric hydrogenation: Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Sausalito, CA, 1999; Chapter 3.2.

[8] Lautens, M.; Rovis, T. *J. Am. Chem. Soc.* **1997**, *119*, 11090−11091.

[9] (a) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Sausalito, CA, 1999; Chapter 2.3. (b) Mann, G.; Hartwig, J. F. *J. Org. Chem.* **1997**, *62*, 5413−5418. (c) Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6054−6058. (d) Saito, S.; Oh-tani, S.; Miyaura, N. *J. Org. Chem.* **1997**, *62*, 8024−8030.

[10] Spielvogel, D. J.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 3500−3501.

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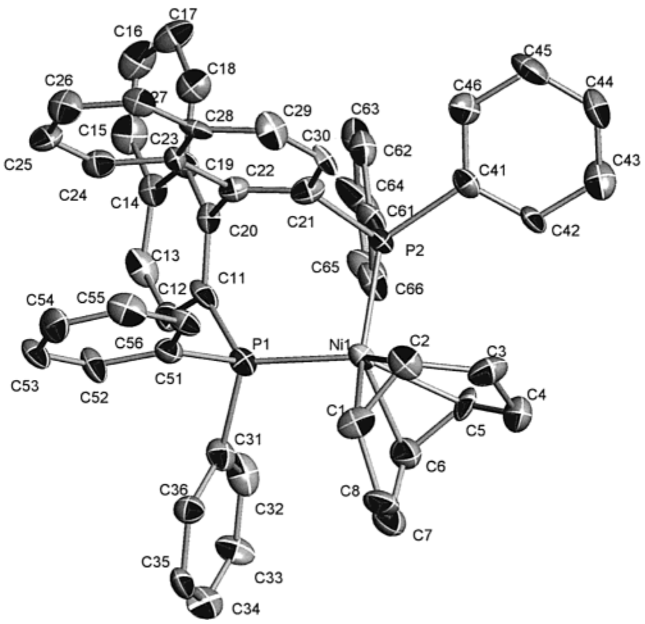

Figure 2. ORTEP drawing of [(*S*)-BINAP]Ni(COD) (**1**) with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for [(*S*)-BINAP]Ni(COD) (1)

Bond Distances			
Ni−C(1)	2.123(9)	P(1)−C(11)	1.851(10)
Ni−C(2)	2.106(9)	P(1)−C(31)	1.829(9)
Ni−C(5)	2.120(8)	P(1)−C(51)	1.845(9)
Ni−C(6)	2.092(10)	P(2)−C(21)	1.807(9)
Ni−P(1)	2.176(3)	P(2)−C(41)	1.869(8)
Ni−P(2)	2.172(3)	P(2)−C(61)	1.821(9)
Bond Angles			
C(1)−Ni−P(1)	97.0(3)	C(1)−Ni−C(5)	93.8(4)
C(1)−Ni−P(2)	139.0(3)	C(1)−Ni−C(6)	84.6(4)
C(1)−Ni−C(2)	38.5(4)	P(1)−Ni−P(2)	97.37(10)

by simple filtration under an inert atmosphere. Recrystallization from toluene/ether/hexane provided burgundy crystals suitable for X-ray analysis. While both the solution and the amorphous, solid material are highly unstable under atmospheric conditions, the prepared crystals proved stable enough to be mounted outside the glovebox. Selected bond distances and angles are summarized in Table 1.

Structural analysis of **1** (see Figure 2) shows the nickel center coordinated in a tetrahedral geometry ($\theta = 83.1°$). The BINAP bite angle (97.37(10)°) lies within the range of the ligand preferred bite angle (92 (±3)°).[11] The Ni−P bond distances (2.1652(8) Å) are in agreement with comparable compounds.[12] Although **1** constitutes the first Ni−BINAP structure to be determined, it would be of great interest to also gain structural information for the Ni−BINAP system in the +2 oxidation state, especially since the important steps in the catalytic cycle (transmetalation, reductive elimination) are initiated from Ni(II) species.[13]

Table 2. Selected Bond Distances (Å) and Angles (deg) for [(*S*)-BINAP]NiBr$_2$ (2)

Bond Distances			
Ni−Br	2.3355(5)	P−C(1)	1.840(3)
Ni−Br(1)	2.3355(5)	P−C(11)	1.823(3)
Ni−P	2.1652(8)	P−C(21)	1.809(3)
Ni−P(1)	2.1652(8)		
Bond Angles			
Br−Ni−Br(1)	96.46(3)	Br−Ni−P(1)	151.95(2)
Br−Ni−P	91.70(2)	P−Ni−P(1)	93.57(5)

[(*S*)-BINAP]NiBr$_2$ (**2**) presents itself as an ideal candidate not only for additional structural insight but also as a potentially useful precatalyst.[14] In situ zinc reduction of **2** yields an active Ni(0)−BINAP catalyst with concomitant formation of a stoichiometric amount of ZnBr$_2$, which is a valuable additive in the arylation chemistry (Figure 1, entry 3). [(*S*)-BINAP]NiBr$_2$ (**2**) is readily prepared by reaction of anhydrous NiBr$_2$ with (*S*)-BINAP in THF at 60 °C. Trituration of the crude material with toluene provided a dark green, air-stable, crystalline material in 88% yield. We were unable to obtain a ^{31}P NMR spectrum, presumably due to the paramagnetic character of **2**; it should also be noted that the ^{1}H NMR signals are significantly broadened.[15] Recrystallization from CH$_2$Cl$_2$/hexane at 4 °C gives nearly black,[16] octahedral crystals suitable for X-ray analysis.

Structural analysis (bond distances and angles are given in Table 2) determined **2** to be C_2 symmetric with the nickel center being coordinated in a strongly distorted square-planar configuration. This is best illustrated by the large dihedral angle (38.3°) between the coordination planes of P−Ni−P(1) and Br−Ni−Br(1) (Figure 3b). Furthermore, the four angles at nickel involving Br, Br(1), P, and P(1) add up to 373.4°.[17] The dihedral angle between the naphthyl planes was determined to be 79.1°. The bite angle of the BINAP ligand (93.57(5)°) lies within the range of the ligand-preferred bite angle (92 (±3)°).[11] It is, however, greatly reduced by comparison to **1**. Notably, the interplanar angle between the two backbone benzene rings in BIPHEMP (bis(diphenylphosphino)biaryl)) complex of Ni(II) is smaller (76.4°) and the bite angle is significantly larger (99.1 (±3)°).[18] The Ni−P (2.1652(8) Å) and Ni−Br (2.3355(5) Å) bond distances are in the typical range for dibromonickel complexes bearing diphosphine ligands.[19] By comparison, [(*R*)-BINAP]PdCl$_2$ exists in a markedly less skewed geometry compared to **2**.[20] It is unclear, however, to what degree this is caused by the halide−halide repulsion (Cl−Cl vs Br−Br)[21] or the metal center (Pd(0) vs Ni(0)) itself.[22]

Initial experiments were undertaken to determine the potential use of [(*S*)-BINAP]NiBr$_2$ (**2**) as a precatalyst

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[11] (a) Van Leeuwen, P. W. N. M.; Kamer, P. C. K.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741−2769. (b) Dierkes, P.; Van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **1999**, 1519−1529. The dihedral angle for **1** between the naphthyl planes was determined to be 75.5°. The COD bite angle in **1** is 92.2°.

[12] Kempe, R.; Sieler, J.; Walther, D. *Z. Kristallogr.* **1996**, *211*, 565−566.

[13] For the proposed catalytic cycle see: Fox, J. M.; Huang, X.; Chieffi, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 1360−1370.

[14] (a) Indolese, A. F.; Consiglio, G. *Organometallics* **1994**, *13*, 2230−2234. (b) Ghosh, A. K.; Matsuda, H. *Org. Lett.* **1999**, *1*, 2157−2159. (c) Majumdar, K. K.; Cheng, C.-H. *Org. Lett.* **2000**, *2*, 2295−2298.

[15] In ref 14b, Ghosh et al. report a ^{31}P signal for [(*R*)-BINAP]NiCl$_2$ at 26.9 ppm. **2** may also exist in a dynamic, conformational equilibrium in solution. Variable-temperature NMR experiments will hopefully bring clarification.

[16] The dark color of the material is in agreement with other known Ni(II) complexes in a tetrahedral distortion.[20]

[17] Near square-planar geometries result in a sum of angles near 360°, while tetrahedral geometries give a sum of angles near 436°.

[18] Knierzinger, A.; Schönholzer, P. *Helv. Chim. Acta* **1992**, *75*, 1211−1220.

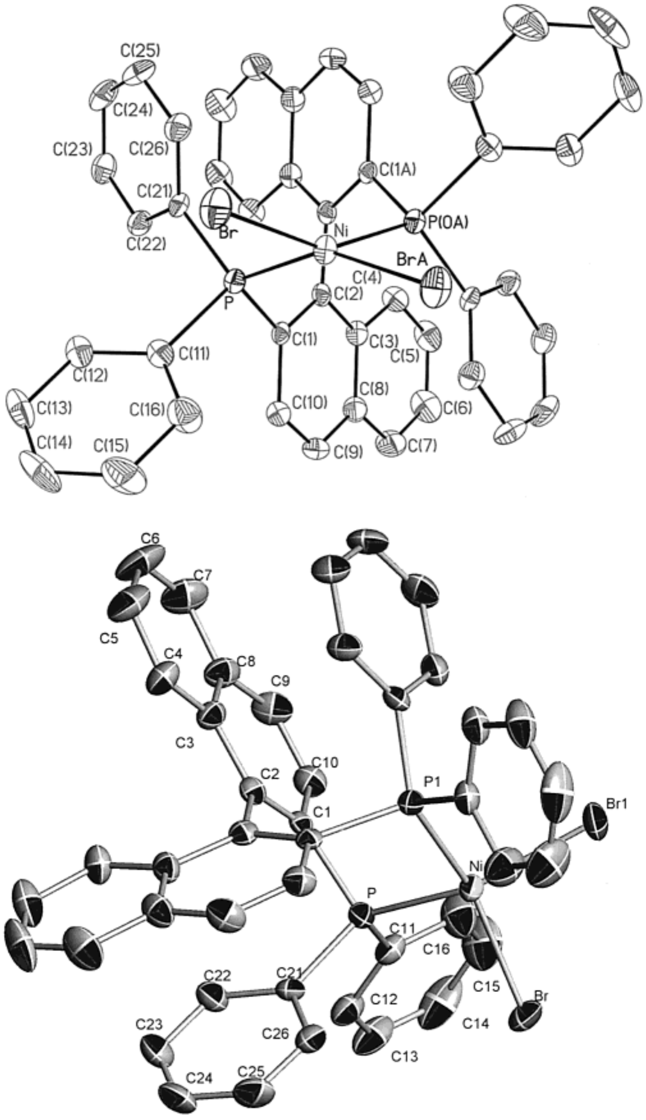

Figure 3. ORTEP drawing of [(*S*)-BINAP]$NiBr_2$ (**2**) with 50% thermal ellipsoids: (a, top) side-on view; (b, bottom) top view. All hydrogen atoms are omitted for clarity.

for the arylation chemistry. Reduction of **2** using excess zinc in THF at 60 °C in the presence of additional (*S*)-BINAP resulted in the formation of a light red solution, which over time turned dark. The one-pot reaction (reduction plus arylation) has so far proven difficult. Arylation of α-methyl-γ-butyrolactone with 3-chloroanisole by this protocol resulted in a poor yield (21%). Fortunately, the enantioselectivity remains high (93% ee, *S* configuration) and the absolute stereochemistry was consistent with the previous results obtained.

Future work will focus on the optimization of a protocol for the efficient in situ reduction of **2** in order to facilitate the use of the Ni−BINAP system for asymmetric catalysis. Furthermore, work is underway to prepare the oxidative-addition product [(*S*)-BINAP]-Ni(Ar)(X). It is hoped that its structural analysis will shed further light on the key steps and intermediates in the catalytic cycle.

Experimental Section

General Comments. Reactions were carried out in oven-dried glassware cooled under argon. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA. IR spectra were recorded with an ASI REACTIR instrument using samples dissolved in dichloromethane. ^1H NMR spectra were recorded at ambient temperature on a Bruker 400 MHz instrument with chemical shifts reported relative to TMS or to the residual solvent peak. ^{31}P NMR spectra were recorded on a Varian 300 MHz instrument with shifts reported relative to H_3PO_4 as an external standard. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter. A standard hemisphere of X-ray data was collected at −90 °C on a Bruker-Nonius SMART/CCD instrument. The structures were solved with direct methods and difference Fourier techniques using SHELXTL. The data were deposited with the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk). Anhydrous toluene, THF, and diethyl ether were purchased from J. T. Baker in CYCLE-TRAINER solvent delivery kegs and vigorously purged with argon for 2 h. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina (for THF) or through neutral alumina and copper(II) oxide (for toluene).[23] The solvents were transferred by syringe from the solvent purification system to the reaction flask. $Ni(COD)_2$ and anhydrous $NiBr_2$ were purchased from Strem Chemical, Inc., stored, and weighed inside a nitrogen-filled glovebox. All chemicals were used without further purification.

Preparation of [(*S*)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl](1,5-cyclooctadienyl)nickel (1). A Schlenk tube equipped with a magnetic stirbar was charged with 274 mg (0.396 mmol) of (*S*)-BINAP and imported into a glovebox, where 100 mg (0.360 mmol) of $Ni(COD)_2$ and toluene (2 mL) were added. The tube was closed with a Teflon screw cap andthe reaction mixture was heated to 60 °C for 10 min and then stirred overnight at room temperature. During the initial heating the reaction mixture turned dark red, and over the course of the reaction, a dark red precipitate formed. The reaction mixture was filtered over a frit (M) and the residue washed with toluene (0.5 mL) to yield 185 mg (65%) of the title compound (**1**) as a red-brown solid. Preparation of single crystals suitable for X-ray studies was performed inside a glovebox. A solution of 30 mg **1** in toluene (0.5 mL) and diethyl ether (0.5 mL) was allowed to vapor-diffuse with *n*-hexane over the course of 4 days to produce deep red platelike crystals. ^1H NMR (C_6D_6, 400 MHz): δ 8.48 (app t, 2H, $J = 8.4$ Hz), 8.07 (app. t, 4H, $J = 7.7$ Hz), 7.60 (app. d, 2H, $J = 8.7$ Hz), 7.41 (app. d, 2H, $J = 8.0$ Hz), 7.35−7.22 (m, 10H), 7.01 (app. t, 2H, $J = 7.1$ Hz), 6.58−6.42 (m, 10H), 8.48 (t, 2H, $J = 8.4$ Hz), 5.02 (m, 2H), 4.87 (m, 2H), 2.14−1.97 (m, 6H), 1.72 (m, 2H). ^{31}P NMR (C_6D_6, 400 MHz): δ 33.7 ppm. Anal. Calcd for $C_{52}H_{44}$-

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(19) (a) [(−)-DIOP]$NiBr_2$: Pilz, F. A.; Frauenrath, H.; Reim, S. *Z. Kristallogr.* **1998**, *213*, 775−776. The structure is reported as distorted tetrahedral: Ni−Br distances 2.338(1) Å, Ni−P distances 2.288(2) Å, Br−Ni−P angle 123.14(5)°. (b) $Ni(PPh_3)_4$: Jarvis, J. A. J.; Mais, R. H. B.; Owston, P. G. *J. Chem. Soc. A* **1968**, 1473−1486. The structure is reported as paramagnetic tetrahedral: Ni−Br distances 2.35(1) Å, Ni−P distances 2.31(1) Å, Br−Ni−Br angle 126°. For comparison, see the following. (c) [(−)-DIOP]$NiBr_2$: Gamlich, V.; Consiglio, G. *Helv. Chim. Acta* **1979**, *62*, 1016−1024. The structure reported is distorted tetrahedral: $Ni-Cl^{1,2}$ distances 2.20(3) Å, $Ni-P^1$ distance 2.30(3) Å and $Ni-P^2$ distance 2.28(3) Å, Cl^1-Ni-P^1 angle 112(3)° and Cl^2-Ni-P^2 angle 99(3)°.

(20) Ozawa, F.; Kubo, A.; Matsumoto, Y.; Hayashi, T. *Organometallics* **1993**, *12*, 4188−4196.

(21) The van der Waals radius for Br is 1.95 Å.[20] The Br−Br distance in **2** is 3.484 Å. The resulting interaction between the halides causes distortion. For $(PPh_3)_2NiBr_2$ the interaction of the p orbitals results in a distorted-tetrahedral geometry: Jarvis, J. A. J.; Mais, R. H. B.; Owston, P. G. *J. Chem. Soc. A* **1968**, 1473.

(22) For ligand field theory as it relates to nickel, see: Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984; Chapter 27.3.4.

(23) (a) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518. (b) Alaimo, P. J.; Peters, D. W.; Arnold, J.; Bergman, R. G. *J. Chem. Educ.* **2001**, *78*, 64.

NiP_2: C, 79.10; H, 5.62. Found: C, 79.01; H, 5.79. Crystal data: $C_{52}H_{40}NiP_2$, $M_r = 785.49$, trigonal, $P3_1$, $a = 10.603(6)$ Å, $\alpha = 90°$, $b = 10.603(6)$ Å, $\beta = 90°$, $c = 30.11(2)$ Å, $\gamma = 120°$, $V = 2931(3)$ Å^3, $Z = 3$, $D_c = 1.335$ Mg/m^3, $\lambda = 0.710$ 73 Å, $T = 183(2)$ K, deep red plates; 5141 independent measured reflections, F^2 refinement, R1 = 0.0681, wR2 = 0.1655, CCDC No. 180383.

Preparation of [(*S*)-(−)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl]nickel(II) Bromide (2). A Schlenk tube equipped with a magnetic stirbar was charged with 220 mg (0.353 mmol) of (*S*)-BINAP and imported into a glovebox, where 70.1 mg (0.321 mmol) of $NiBr_2$ (anhydrous) and THF (2 mL) were added. The tube was closed with a Teflon screw cap and the reaction mixture heated to 60 °C for 24 h. During the course of the reaction the initially brownish slurry turned dark green, and some dark green precipitate formed. The reaction mixture was cooled to room temperature. After removal of the solvent under reduced pressure the dark green residue was triturated with toluene (2.5 mL). Filtration over a medium frit yielded 237 mg (88%) of the title compound as a fine crystalline, dark green, air-stable material. For the preparation of single crystals several drops of hexane were added to a nearly saturated solution of **2** in dichloromethane (0.2 mL). The crystals were allowed to grow at 4 °C over the course of 3 days. Mp: >250 °C (toluene). ^1H NMR ($CDCl_3$, TMS, 400 MHz): δ 9.29 (bs, 4H), 8.72 (bs, 2H), 8.28 (m, 5H), 8.14 (bs, 5H), 7.87 (bs, 4H), 7.65 (m, 2H), 6.60 (m, 4H), 6.03 (bs, 2H), 5.80 (m, 2H), 5.49 (m, 2H). IR (cm^{-1}): 1501, 1482, 1437, 1314, 1098, 1027, 999, 872, 818. $[\alpha]^{20}_D = -230.9°$ (c = 0.55, CH_2Cl_2). Anal. Calcd for $C_{44}H_{32}Br_2NiP_2$: C, 62.83; H, 3.83. Found: C, 63.05; H, 3.99. Crystal data: $C_{44}H_{32}Br_2NiP_2$, M_r = 841.17, tetragonal, $P4_32_12$, $a = 11.7738(11)$ Å, $\alpha = 90°$, $b = 11.7738(11)$ Å, $\beta = 90°$, $c = 26.137(4)$ Å, $\gamma = 90°$, $V = 3623.1(7)$ Å^3, $Z = 4$, $D_c = 1.542$ Mg/m^3, $\lambda = 0.710$ 73 Å, $T = 183(2)$ K, dark green octagons; 2619 independent measured reflections, F^2 refinement, R1 = 0.0236, wR2 = 0.0539, CCDC No. 180470.

Preparation of (−)-(*S*)-3-(3-Methoxyphenyl)-3-methyldihydrofuran-2-one (Figure 1, Entry 3). An oven-dried, resealable Schlenk tube containing a magnetic stirbar was cooled to room temperature and then was charged with (*S*)-BINAP (13.2 mg, 21.3 μmol). The tube was sealed, evacuated, and back-filled with argon. From a freshly prepared, yellow, homogeneous stock solution of $Ni(COD)_2$ (0.05 M, toluene), 250 μL (12.5 μmol) was added by syringe while purging with argon. The tube was sealed and heated to 60 °C for 5 min, during which time the solution turned dark red. The reaction vessel was removed from the oil bath, and sequentially α-methyl-γ-butyrolactone (47.0 μL, 0.5 mmol), dodecane (50 μL, internal standard), and NaHMDS (105.4 mg, 0.575 mmol) were added under argon. From a stock solution, $ZnBr_2$ (0.51 M, THF), 250 μL (37.5 μmol) was added by syringe while purging with argon; the mixture was then stirred for 5 min at room temperature. 3-Chloroanisole (30.6 μL, 0.25 mmol) (0.25 mmol) was added by syringe followed by the addition of toluene (500 μL) while purging with argon. The tube was sealed and heated to 60 °C for 20 h. After complete conversion had been accomplished, as judged by GC analysis, the reaction mixture was cooled to room temperature and was then filtered through a pad of silica gel (3 × 0.5 cm) with ethyl acetate as eluent. The eluate was concentrated under reduced pressure. Chromatography (1.5 × 30 cm, ethyl acetate/hexane 1/4) of the crude mixture on silica yielded 42.6 mg (83%) of the title compound as a colorless oil. ^1H NMR ($CDCl_3$, TMS, 400 MHz): δ 7.30 (m, 1H), 6.99 (m, 2H), 6.84 (m, 1H), 4.34 (ddd, 1H, J = 9.0, 7.8, 3.9 Hz), 4.16 (ddd, 1H, J = 8.9, 8.9, 6.5 Hz), 3.82 (s, 3H), 2.69 (ddd, 1H, J = 12.9, 6.5, 3.9 Hz), 2.41 (ddd, 1H, J = 12.9, 8.7, 7.8 Hz), 1.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.3, 160.3, 143.0, 130.3, 118.5, 112.8, 112.6, 66.7, 65.5, 55.7, 47.9, 38.5, 25.9. IR (cm^{-1}): 2975, 2941, 2916, 1769, 1602, 1584, 1490, 1453, 1382, 1293, 1241, 1223, 1200, 1175, 1084, 1048, 1032, 783, 737. $[\alpha]^{20}_D = -7.3°$ (c = 2.5, CH_2Cl_2). HPLC (DAICEL OD column): t_{major} = 13.7 min, t_{minor} = 17.0 min (10% iPA/Hex, 0.7 mL/min), 96% ee. Anal. Calcd for $C_{12}H_{14}O_2$: C, 69.88; H, 6.84. Found: C, 69.58; H, 6.91.

One-Pot Protocol for the in Situ Zinc Reduction−Arylation. An oven-dried, resealable Schlenk tube containing a magnetic stirbar was cooled to room temperature and then was charged with (*S*)-BINAP (20.4 mg, 39 μmol), [(*S*)-BINAP]-$NiBr_2$ (40.8 mg, 48 μmol), and zinc dust (6.3 mg, 97 μmol). The tube was sealed, evacuated, and back-filled with argon. While purging with argon, THF (250 μL) was added by syringe. The tube was sealed and heated to 60 °C for 5 min, during which time a homogeneous, red solution (with some visible zinc dust remaining) formed. The reaction vessel was removed from the oil bath, and sequentially 3-chloroanisole (30.6 μL, 0.25 mmol) and dodecane (50 μL, internal standard) were added under argon. After 5 min at room temperature α-methyl-γ-butyrolactone (47.0 μL, 0.5 mmol), NaHMDS (105.4 mg, 0.575 mmol), and toluene (750 μL) were added while purging with argon. The tube was sealed and heated to 60 °C for 20 h. The reaction mixture turns dark upon addition of the base. The reaction mixture was cooled to room temperature and was then filtered through a pad of silica gel (3 × 0.5 cm) with ethyl acetate as eluent. The eluate was concentrated under reduced pressure. Chromatography of the residue on silica gel (1.5 × 30 cm, ethyl acetate/hexane) yielded 10.8 mg (21%) of the title compound as a colorless oil. Spectral and GC data are identical with those of previously prepared material.

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Supporting Information Available: Details about the X-ray crystal structures, including ORTEP diagrams and tables of crystal data and structure refinement details, atomic coordinates, bond lengths and angles, and isotropic and anisotropic diplacement parameters for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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